Performance of Concrete with Increased Acid Resistance for Natural Draught Cooling Towers

Carsten RIECK[1], Roland HÜTTL[1]and Dieter BUSCH[2]

[1] *Kiwa MPA Bautest GmbH, Berlin, Germany*
[2] *ZERNA Planen und Prüfen GmbH, Bochum, Germany*

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ABSTRACT: The construction of the first cooling tower shell of concrete with increased acid resistance started at the RWE power station of Niederaußem near Cologne in 1999. Since then, many electricity producing companies built natural draught cooling towers with this innovative concrete technology in Germany: Neurath (RWE), Datteln (E.ON), Boxberg (Vattenfall), Lünen (Trianel) and Westfalen (RWE). The paper describes the specification of the concrete, the development of the concrete technology from the construction of Niederaußem until today and as well the performance test for the concrete in the laboratory and the quality check during the construction. Recent investigative results show the performance of the concrete with increased acid resistance at various pH values (2.5 / 3.5 / 4.5) over one year.

1 ACID-CORROSION OF CEMENT-BOUND MATERIALS

In Germany it is state of the art for over 25 years that the flue gases are discharges via the cooling tower, when a new power station is built. This means a very aggressive environment for the concrete of the inner shell of the cooling tower. To avoid an expensive and time-consuming coating of the inner shell of the cooling tower, a concrete with increased acid resistance was developed in connection with the building of the highest cooling tower of the world in Niederaußem in 1999. This concrete should resist the aggressive conditions in the cooling tower without coating for at least 40 years.

Concrete is severely damaged in particular by acids. Since concrete aggregates are virtually insoluble in acids (with the exception of limestone), the acids chiefly attack the cement stone matrix. Acids dissolve almost all components of the hardened cement paste matrix (CSH phases, $Ca(OH)_2$), forming soluble salts of calcium, aluminium and iron as well as silicic acid. The calcium hydroxide ($Ca(OH)_2$) produced during the hydration of Portland cement (CEM I) – which makes up 15 to 25 % by mass of the cement stone – is particularly acid-soluble. Calcium hydroxide crystallises out during the hydration of cement mainly in those areas that were previously occupied by the mixing water, as well as on the surfaces of the aggregates. A three-dimensional cross-linked $Ca(OH)_2$ structure is created that runs right through the entire concrete. Fig. 1 shows a photo of a hardened cement stone matrix taken with a polarizing microscope. The CSH phases and clinker grains (unhydrated cement) are black, the light $Ca(OH)_2$ (yellow) can be distinguished.

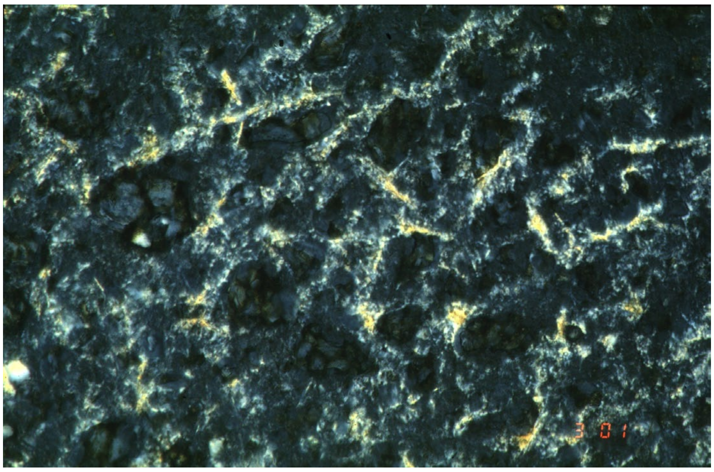

Figure 1: Photo of the three-dimensionally cross-linked calcium hydroxide microstructure taken with a polarising microscope

If the calcium hydroxide is dissolved by acid, then the corrosion penetrates very quickly along these tracks into the depth of the binding agent matrix. Initially a purely visual, undetectable deep damage occurs in the concrete. A further reason for the fast corrosion by acid is Grotthus' transport mechanism for H^+ ions (acid ions), see Fig. 2. It is approx. five times faster than conventional ion diffusion. In the case of the acid corrosion in a cooling tower, the sulphate ions from the sulphuric acid then penetrate the concrete along the dissolved $Ca(OH)_2$ tracks in a second step and further destroy the concrete through a sulphate attack. The concrete matrix damaged by sulphuric acid (H_2SO_4) accordingly possesses two damage fronts: within the first damage front, viewed from the damaged surface, the concrete matrix is completely destroyed by dissolving attack (H^+) and sulphate attack ($SO_4{}^{2-}$). This completely destroyed layer is relatively easy to remove mechanically, if it does not drop off on its own.

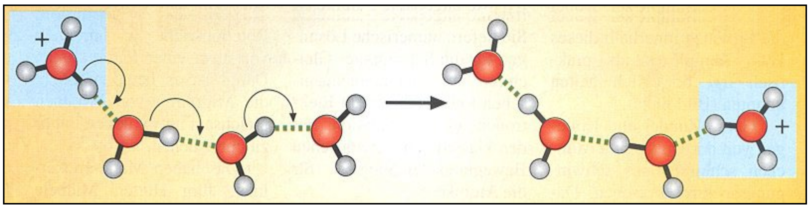

Figure 2: Grotthus' transport mechanism for H+ ions (acid ions), from: Marx, D.: Proton migration in the virtual laboratory. In: Spektrum der Wissenschaft, July 1999, p. 21-24

Invisible to the human eye and only detectable by microscope is the second damage front, which runs more deeply. Within this second layer, the acid has damaged the concrete matrix only by dissolving attack. The mechanical stability of this layer is largely retained, since no or hardly any sulphate attack has taken place yet. Since the acid encounters unhydrated cement clinker grains, these are now hydrated. This results in a change of volume and hence, the formation of microcracks. In addition, the hydration releases alkalis that counteract the lowering of the pH value due to the acid. Therefore, this damage front can neither be detected by sulphate drill dust analyses nor by the use of phenolphthalein. Fig. 3 shows the scanning electron microscope photo (backscattering electron image) of a mortar damaged by sulphuric acid, with both damage fronts. The area of deep damage is only very small in concretes with optimised acid resistance.

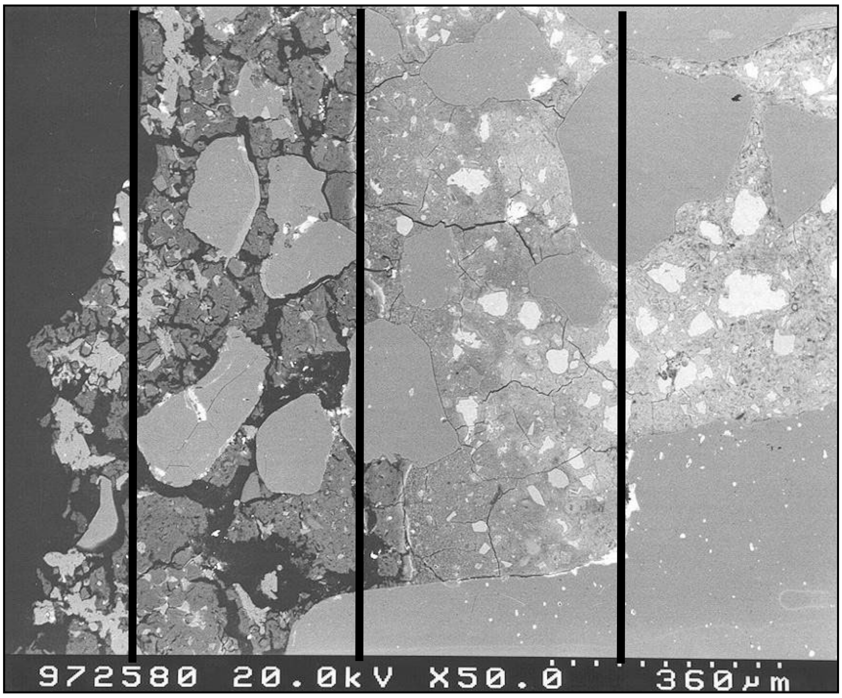

Figure 3: Scanning electron microscopic photo of a mortar damaged by sulphuric acid, with the two damage fronts. The aggregate is dark grey, while the unhydrated cement clinker grains are white.

In the case of concretes whose acid resistance is not optimised, severe damage of the concrete down to the depth of the reinforcement can occur within a few years, depending on the conditions in the cooling tower, so that stability is no longer ensured well before the end of the planned service life of the cooling tower.

2 PERFORMANCE TESTS AND QUALITY MANAGEMENT

2.1 *Test Procedure*

For the quality assurance of the characteristic ‘increased acid resistance’ in cement-bound building materials, in particular concrete, a test procedure with the associated evaluation criteria which – modified in relation to the project – is usually stipulated by the respective builder in the tendering specifications, has proven effective, since there are no adequate specifications for the characteristic ‘increased acid resistance’ in standards or directives in Germany. The programme presented in Tab. 1 for the examination of the chemical resistance of concretes to acids and impermeability to harmful substances was developed with the help of a multitude of research projects as well as through many years of investigation by the

Technical University of Berlin (Prof. Dr. B. Hillemeier), the Gesellschaft für Materialprüfung und Baustoffforschung (MBF - Material Testing and Building Material Research Company), the Materialprüfungsanstalt MPA Berlin-Brandenburg (Institute of Material Testing, Berlin-Brandenburg) and the Kiwa MPA Bautest and has been used successfully for over ten years in the construction of power station cooling towers, wastewater treatment plants and other structures.

Measured variable	**Limit values for concretes with highest resistances**	**Typical values for 'SRB 85/35' (reference concrete)**
Acid resistance Kiwa MPA Bautest method	max. 10 % greater damage depths than 'SRB 85/35'	Damage depth 1.1 mm to 1.3 mm (12 weeks H_2SO_4, pH 3.5)
Sulphate resistance SVA method	Longitudinal strain of test specimen < 0.5 mm/m	Longitudinal strain of test specimen < 0.1 mm/m
Total porosity from gross and true density	< 11 % by vol.	9 - 10 % by vol.
Cumulative pore volume r < 0,1 mm, (Hg pressure porosimetry)	< 40 mm^3/g	20 to 30 mm^3/g
Average pore radius r < 0,1 mm, (Hg pressure porosimetry	< 0.1 µm	0.02 to 0.04 µm
Chloride migration coefficient Method according to Tang & Schiessl	< 1.0×10^{-12} mm^2/s	0.4 to 0.6×10^{-12} mm^2/s
Freedom from micro-cracks, frost/de-icing resistance CDF method with 56 cycles	Decrease in the dyn. modulus of elasticity < 40 %, mass loss < 1500 g/m^2	Decrease in the dyn. modulus of elasticity 10 to 30 %, mass loss 400 - 1200 g/m^2
Residual alkalinity $Ca(OH)_2$ content by thermogravimetry	> 2.5 g $Ca(OH)_2$ per 100 g binding agent	7-9 g $Ca(OH)_2$ per 100 g binding agent

Table 1: Test criteria and limit values for concretes with maximum resistances (to be defined for the specific project) and typical measured values for 'SRB 85/35' (reference concrete)

The suitability of a concrete recipe with regard to increased acid resistance can be tested with the help of this performance test. This test is connected with an extensive initial test of the concrete raw materials and the fresh concrete characteristics. For the purposes of quality assurance, the crucial characteristics of the concrete raw materials are checked at specified intervals during manufacturing or in the construction phase, as the case may be, in order to be able to ensure constant quality of the concrete. These QA measures are usually also demanded and checked by the builder.

Using the test procedure presented here, it is possible to determine the resistance and impermeability of concretes and other cement-bound systems, e.g. mortar systems, to harmful media, in particular sulphuric acid, sulphate and chloride, as well as the 'matrix quality' of the recipes. The term 'matrix quality' refers to the freedom of the binding agent matrix from microcracks, which has a decisive influence on the long-term resistance. The freedom from microcracks is thereby determined by means of determining the frost (de-icing salt) resistance as an auxiliary variable.

The test procedure consists of the individual tests listed below. For each test, the limit values are specified with which a concrete recipe must comply in its entirety without exception in order to be considered to be a recipe of the highest resistance and impermeability. The limit values are each slightly higher than the maximum values that a concrete (on the basis of Portland cement as a hydraulic binding agent) can reach in the light of experience.

2.2 *Acid resistance*

The test of the resistance of the concretes to sulphuric acid takes place according to the test method of the Kiwa MPA Bautest: according to this test method, the acid resistance is determined following storage of concrete test specimens for 12 weeks in sulphuric acid, usually with a pH of 3.5, see Fig. 4. The loss of mass of the test specimens is determined with and without the simulation of additional abrasive erosion (weekly removal of the surface coatings). Subsequently, the erosion and damage depths of the test specimens with simulation of additional abrasive erosion are determined using a stereo or polarizing microscope. The test takes place in comparison with the reference concrete 'SRB 85/35' with optimised acid resistance, for which more than ten years' worth of experience values is available. The concrete tested must exhibit an acid resistance that may only be 10 % worse than that of the 'SRB 85/35' concrete with regard to the microscopically determined damage depth. On average, damage depths of approx. 1.1 to 1.3 mm are measured with this method for the 'SRB 85/35' concrete at a pH value of 3.5.

Figure 4: Storage of concrete test specimens for 12 weeks in sulphuric acid, usually with a pH of 3.5

2.3 *Sulphate resistance*

The sulphate resistance is tested in accordance with the SVA method (Deutsches Institut für Bautechnik 1998) on flat mortar prisms with the planned binding agent composition (standard mortar, w/c_{eq} value = 0.5). The longitudinal strain of the flat mortar prisms due to storage in sulphate solution must be less than 0.5 mm/m after 91 days.

2.4 *Impermeability to dissolved harmful substances (porosity)*

In order to determine the porosity of the concretes, the total porosity from the gross and true density is determined in addition to the cumulative pore volume and the pore size distribution in the pore range with the radius < 100 µm (0.1 mm) by means of mercury pressure porosimetry. The total porosity of the concrete, determined from the gross and true density, must by less than 11 % by vol. The cumulative pore volume of the concrete in the pore range < 100 µm (0.1 mm), determined by means of mercury pressure porosimetry, must be less than 40 mm^3/g, the average pore radius less than 0.1 µm.

2.5 *Impermeability to chloride*

In order to determine the impermeability of the concretes to the penetration of chlorides (danger of pitting corrosion of the steel reinforcement) the chloride diffusion coefficient is measured by means of the chloride migration method according to (Tang & Nilsson 1991) and (Schiessl & Wiens 1997). The chloride diffusion coefficient must be less than 1.0×10^{-12} m^2/s.

2.6 *Freedom of the binding agent matrix from microcracks via the frost de-icing salt resistance*

Freedom of the concretes from micro-cracks is tested on the basis of the CDF method of the RILEM Draught Recommendation 117-FDC, but with 56 frost/de-icing salt cycles instead of 28. The test specimens are not manufactured with Teflon inserts, but cut from cubes, so that the concrete matrix is tested and not the formed surface. If a microcrack microstructure exists, the frost de-icing salt resistance decreases sharply over the course of the test. The decrease in the dynamic modulus of elasticity, measured with the help of the ultrasonic running times, may not be greater than 40 %. The loss of mass of the concrete may not be greater than 1,500 g/m^2. A further evaluation criterion is whether the weathering, in particular after approximately 35 to 45 frost/de-icing salt cycles, increases or whether the total weathering process is linear. If the weathering increases disproportionately in this area, this is a sign of an existing microcrack microstructure.

2.7 *Corrosion protection of the steel reinforcement (residual alkalinity)*

In concretes with increased acid resistance, the portion of the calcium hydroxide that is soluble in acid is minimised by concrete technology. In order nevertheless to protect the reinforcing steel sufficiently against corrosion, the residual alkalinity of the concrete is determined. This is done with the aid of thermogravimetry. The residual alkalinity after 91 days may not be less than 2.5 g $Ca(OH)_2$ per 100 g binding agent.

The test criteria with the associated limit values are summarised in Tab. 1. The ‘SRB 85/35’ concrete, with the maximum possible impermeability and resistance, is used as a reference concrete, in particular for acid resistance. Therefore, the values typically determined with the ‘SRB 85/35’ concrete are additionally listed in Tab. 1.

3 THE COOLING TOWER IN NIEDERAUßEM AND THE DEVELOPMENT OF CONCRETE TECHNOLOGY SINCE THEN

The construction of the first cooling tower shell of concrete with increased acid resistance started at the RWE power station of Niederaußem near Cologne in 1999. This type of concrete was developed after four years of research to avoid coating of the inner cooling tower shell due to the discharge of flue gases via the cooling tower. Intensive planning and tests of materials and construction concepts by the construction company in cooperation with the persons responsible for the quality assurance made it possible to build the cooling tower in Niederaußem without problems and to keep the schedule. Carefully planned quality measures during the construction and a monitoring system proofed the assumptions. These positive experiences led RWE Power to build more cooling towers of this type.

In principle, the chemical resistance of concretes and mortars can be greatly increased if the three-dimensional cross-linked calcium hydroxide microstructure of the cement stone matrix is interrupted and the $Ca(OH)_2$ is limited to a sensible amount. The most frequently employed method of limiting or converting the $Ca(OH)_2$ content and to interrupt the three-dimensionally cross-linked $Ca(OH)_2$ microstructure is to use mineral admixtures, chiefly blast furnace sand, fly ashes and microsilica. The admixtures convert the $Ca(OH)_2$ into the more resistant CSH phases by means of the puzzolanic or latent hydraulic reaction. Apart from the stability of the binding agent matrix, the granulogical gradation of the components of the concrete must be optimised. Above all, a complete gradation in the ultra-fine range is important for the tightness of the matrix.

The development of concretes with increased acid resistance began more than ten years ago with recipes on the basis of Portland cement (CEM I), fly ash and microsilica. These initially poorly robust mixtures have been continuously developed and are still used successfully today. These were followed by concrete recipes with ultra-fine fly ash and most recently with alumo layer silicates. Concrete with increased acid resistance can also be manufactured with CEM II and CEM III, so that there are hardly any restrictions in the choice of cement. Ultimately the decisive factor is the performance, which is tested using the examination programme described above.

With concretes optimised for acid-resistance, the shell of cooling towers or precast elements can be built without coating with the normally demanded service lifetimes, provided that the pH value of the acid corrosion does not sink permanently below 3.5. Lower pH values may also briefly prevail.

Concrete with increased acid resistance, tested in accordance with the Kiwa MPA Bautest examination programme, can be purchased in Germany today from various suppliers in the form of ready-mix concrete, as precast elements or as pipes and manholes. Builders, planners, building firms and pipe manufacturers are thus offered various possibilities of using the advantages of concrete with increased acid resistance. Concrete with increased acid resistance has now been used in eight cooling towers in Germany. Almost all German main power station operators utilise the advantages of this building material.

4 LONG DURATON TEST

Within a research project sponsored by RWE, the acid resistance of the concrete with increased acid resistance used in Neurath was tested at various pH values (2.5 / 3.5 / 4.5) for 12 months. The erosion and damage depths of the test specimens determined by using a stereo and polarizing microscope are illustrated in Fig. 5. The erosion and damage depths can be characterized approx. by a square root of time equation. The difference between pH 4.5

and pH 3.5 is low, but the difference between pH 3.5 and pH 2.5 is high. These results bring out again the above mentioned critical value of pH 3.5 for concrete with increased acid resistance and correspond to the practical experience from the cooling tower in Niederaußem.

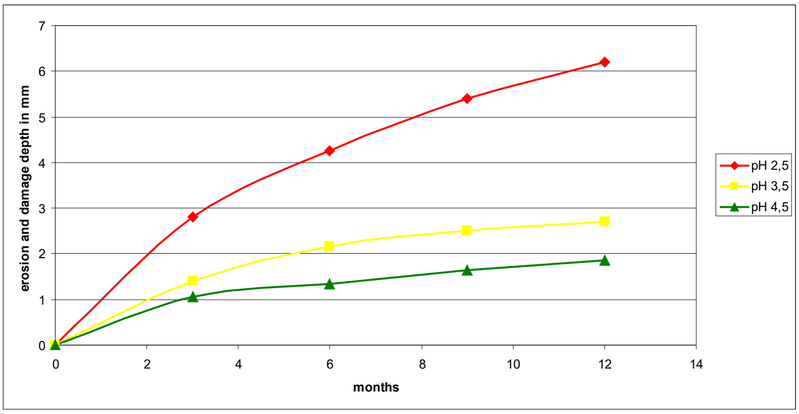

Figure 4: Erosion and damage depths of concrete with increased acid resistance

5 SUMMARY

The paper describes the acid-corrosion of cement-bound materials, the development of the concrete technology from the construction of Niederaußem until today and as well the performance test for the concrete in the laboratory. Recent investigative results show the performance of the concrete at various pH values over one year.

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